

The Role of Non-Equilibrium Carriers in Formation of Thermo-E.M.F. in Bipolar Semiconductors

Yu. G. Gurevich,* G. N. Logvinov,[†] and I. N. Volovichev[‡]

*Departamento de Física, CINVESTAV—IPN,
Apdo. Postal 14-740, 07000 México, D.F.*

G. Espejo[§]

*CICATA—IPN, García Obeso 306, Col. Centro,
58000, Mor., Mich., México.*

O. Yu. Titov[¶]

*CICATA—IPN, José Siurob 10, Col. Alameda,
76040 Santiago de Querétaro, Qro., México.*

A. Meriuts**

Kharkov Politechnical University, Kharkov 310002, Ukraine.

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It is presented a new approach to thermoelectric phenomena, as a linear transport process of non-equilibrium charge carriers. The role of non-equilibrium carriers, as well as surface and bulk recombination, has shown to be crucial even within a linear approximation. Electron and hole Fermi quasi-levels that appeared in a thermal field are calculated for the case of thermoelectric current flow through a circuit and the corresponding boundary conditions are obtained. It is shown for the first time, that the Fermi quasi-level of one of the subsystems of quasi-particles, can be a non-monotonic function of the coordinates. General expressions for the thermoelectric current, thermo-e.m.f., and electrical resistance of bipolar semiconductors have been obtained. For the first time, surface recombination and surface resistance were taken into account in thermoelectric phenomena.

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I. INTRODUCTION

The critical treatment of the generally accepted theory of thermo-e.m.f. in bipolar semiconductors was presented in theoretical works by Gurevich *et al.*^{1,2} The calculations were carried out without recombination term (the scope of those papers was intentionally limited to explain the correct definition of thermo-e.m.f.).

We will continue our constructive criticism (as we will offer some practical solutions) with following, never-discussed facts.

The first of them is related to applied temperature difference. As soon as we have the temperature gradient, both electrons and holes diffuse from the hot end of the sample to the cold one. As a result, electron and hole concentrations should increase on the cold end of the sample if recombination processes are ignored (usually they even were not discussed in the study of thermoelectric phenomena,³ and corresponding terms were not presented in the equations. Therefore one can say that recombination was ignored.).

As a consequence, the well known correlation³

$$n_0 p_0 = n_i^2 \quad (1)$$

is violated, where n_0 , p_0 are equilibrium electron and hole concentrations at some equilibrium temperature, n_i is the intrinsic concentration in the same semiconductor.

The fact that Eq. (1) be correct, is based on the existence of common Fermi levels for electrons and holes and the equality

$$\mu_n^0 = -\varepsilon_g - \mu_p^0, \quad (2)$$

always suits in this case. Here μ_n^0 , μ_p^0 are electron and hole chemical potentials in equilibrium state, ε_g is the energy gap.

So if equation (1) is not fulfilled, then $\mu_n \neq -\varepsilon_g - \mu_p$, where μ_n and μ_p are the non-equilibrium electron and hole chemical potentials. This means that the common Fermi level is splitted and two Fermi quasi-levels (electron and hole) originate.

Since the internal thermoelectric field is determined by the gradient of electrochemical potential,⁴ the question that immediately arose was: Which field shall we use to calculate thermo-e.m.f.: $E_1 = -\nabla(\varphi - \mu_n/e)$ or $E_2 = -\nabla(\varphi + \mu_p/e)$? Here, φ is the electrical potential caused by the redistribution of electric charges in the thermal field, and $-e$ is the electron charge. Besides, recombination processes shall be taken into account if there appear non-equilibrium carriers.

The second aspect is related to the way that thermo-e.m.f. is usually calculated in an open circuit. At the same time, it is well known that the correct definition of e.m.f. of any nature shall be related to a closed circuit. This circumstance is especially important to determine thermo-e.m.f. in bipolar semiconductors. It is enough to imagine the particular special situation with inhomogeneously heated p -type semiconductor closed with the metal section of circuit. There are no holes in the metal and there are no electrons in a p -type semiconductor. The explanation of this phenomena can not be defined within the limits of thermoelectric traditional theory. It is clear that it is necessary to use boundary conditions taking into account current flux and surface recombination processes. Nobody had done that before.

The third aspect is that the consideration of thermo-e.m.f. in bipolar semiconductors is carried out, usually, after the study of this problem in unipolar semiconductors, and many results are obtained “by analogy.” Methodically it ought to be done starting from “point zero” to avoid a series of mistakes and incorrect judgments.

There are more aspects related with this problem but it is clear that one of the main problems when establishing a correct theory of thermo-e.m.f. in bipolar semiconductors is the successive accounting of the non-equilibrium carriers in electric and thermal currents caused by inhomogeneous heating of the semiconductor.

This problem has been partially studied;^{1,2} however, new ideas have arisen: the modernization in description of recombination processes, the accurate definition of current boundary conditions, calculation of spatial dependencies of Fermi quasi-levels, consideration of general expressions for thermo-e.m.f., etc...

The need of more precise theories and the generalization of some results, considered earlier, have just appeared.

Covering all aforementioned problems is beyond the scope of present work. We will only expatiate on those of common interest.

II. THE MAIN EQUATIONS OF THE PROBLEM

Let us consider the model of thermoelectric circuit, consisting of an isotropic, homogeneous bipolar semiconductor, of parallelepiped form, closed by a metal section with an electrical conductivity σ_m , length L (see Fig. 1) and unit cross-section. The resistance of external circuit (including voltmeter's resistance) is $R_{ex} = L/\sigma_m$. The metal-semiconductor

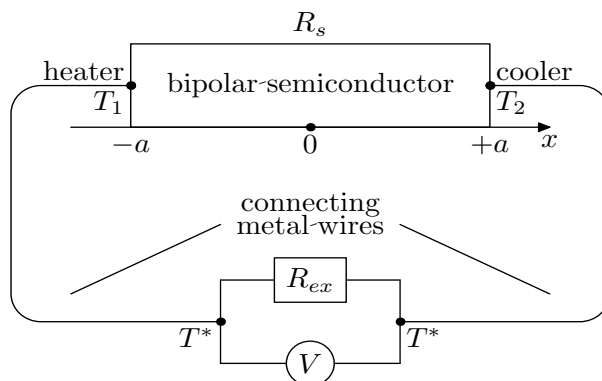


FIG. 1: Electrical circuit for the measurement of thermo-e.m.f., R_s is the semiconductor resistance.

contact on the left, $x = -a$, is kept under a temperature T_1 ; at $x = +a$ is at a temperature $T_2 < T_1$. Here and below, temperature is expressed in energy units, *i. e.* Boltzmann's constant is equal to unit. The lateral sides are thermally insulated, so the problem is unidimensional. We suppose that the temperature difference $\Delta T = T_1 - T_2$ is small enough [$\Delta T/T^* \ll 1$, $T^* = (T_1 + T_2)/2$], so the problem is linear. The thermal contacts between metal and semiconductor are assumed to be isothermal, for simplicity. We also assume that non-equilibrium temperatures of all quasi-particle subsystems (electrons, holes and phonons) taking part in heat transport are the same.

Under these conditions, the temperature field in the semiconductor is represented by the function

$$T(x) = T^* - \frac{\Delta T}{2a}x. \quad (3)$$

At stationary state, the thermo-e.m.f. is generated in the circuit and the constant thermoelectric current j_0 flows through it. In bipolar semiconductors,

$$j_0 = j_n + j_p, \quad (4)$$

where

$$\begin{aligned} j_n &= -\sigma_n \left(\frac{d\tilde{\varphi}_n}{dx} + \alpha_n \frac{dT}{dx} \right), \\ j_p &= -\sigma_p \left(\frac{d\tilde{\varphi}_p}{dx} + \alpha_p \frac{dT}{dx} \right) \end{aligned} \quad (5)$$

are the partial electron and hole currents; σ_n , σ_p are the bulk electron and hole electrical conductivities; α_n , α_p are the electron and hole thermoelectric powers; $\tilde{\varphi}_{n,p} = \varphi \mp \mu_{n,p}/e$ are the electrochemical electron and hole potentials (Fermi quasi-levels).

The equations of continuity for partial currents j_n and j_p are:

$$\frac{dj_n}{dx} = eR_n, \quad \frac{dj_p}{dx} = -eR_p, \quad (6)$$

where $R_{n,p}$ are bulk recombination rates.

In accordance with Eq. $\frac{\partial \rho}{\partial t} = -\text{div } \mathbf{j}$ (the consequence of Maxwell equation) in the static case we obtain,

$$\text{div } \mathbf{j} = \text{div } (\mathbf{j}_n + \mathbf{j}_p) = 0. \quad (7)$$

where ρ is charge density, \mathbf{j} is the total current.

Let us note that Eqs. (6) and (7) are independent, so the electron and hole bulk recombination rates (R_n , R_p) must be the same.⁵

By itself, the correct description of the recombination term $R_{n,p}$ in Eq. (6) is a serious problem in the presence of temperature fields. The frequently used form for R : $R_n = \delta n/\tau_n$, $R_p = \delta p/\tau_p$ does not ensure the identical equality of the recombination rates of electrons and holes for any recombination mechanism. In its turn, non-equal recombination rates do not preserve the total charge [see Eq. (7)]. Moreover, treating the equality $R_n = R_p = \delta p/\tau_p$ as an additional condition to find the non-equilibrium concentration, makes no physical sense.^{5,6}

It is necessary to use the expression obtained from statistical consideration of electron transitions between valence and conduction bands (or the Shockley-Read expression for recombination through impurity levels) to obtain a correct description of recombination.^{5,6}

For the first case, for example, $R_n \equiv R_p = k(np - n_i^2)$ (where k is the capture factor, $n = n_0 + \delta n'$, $p = p_0 + \delta p'$), $\delta n'$, $\delta p'$ are non-equilibrium additions to the equilibrium concentrations n_0 and p_0 .

Assuming $\delta n' \ll n_0$, $\delta p' \ll p_0$ and linearizing the recombination rate expression, we get

$$R = R_n = R_p = \frac{\delta n'}{\tau_n} + \frac{\delta p'}{\tau_p}, \quad (8)$$

where $\tau_n = (kp_0)^{-1}$, $\tau_p = (kn_0)^{-1}$.

The values τ_n and τ_p have dimensions of time but have not some physical sense for the general case ($\delta n' \neq \delta p'$). Only if the condition of quasi-neutrality is fulfilled,⁷ ($\delta n' = \delta p'$), the uniform time $\tau^{-1} = \tau_n^{-1} + \tau_p^{-1}$ can be introduced, which has the sense of life-time of non-equilibrium carriers.

Equation (6) must be supplemented by the necessary boundary conditions. Since holes can not pass through semiconductor-metal contacts, boundary conditions for them are:

$$j_p|_{x=\mp a} = \mp eR_s, \quad (9)$$

where R_s is the surface recombination rate.

The boundary conditions for the electron current j_n , taking into account Eq. (4), are in the form

$$j_n|_{x=\mp a} = j_0 \pm eR_s. \quad (10)$$

Similarly to the bulk recombination, the expressions for surface recombination must be written in the following form:

$$R_n^s = R_p^s = R_s = S_n \delta n' + S_p \delta p', \quad (11)$$

where S_n and S_p are some coefficients which characterize the properties of semiconductor surface. Only when the quasi-neutrality condition takes place ($\delta n' = \delta p'$), the value $S = S_n + S_p$ acquires the sense of surface recombination velocity, and

$$R_s = S\delta n'. \quad (12)$$

It should be noted that the full current j_0 satisfies the following condition at the metal-semiconductor contacts:²

$$j_0 = \pm \sigma_n^{s\pm} [\varphi_s(\pm a) - \varphi_m(\pm a)] \mp \frac{\sigma_n^s}{e} [\mu_n^s(\pm a) - \mu_m] \pm \frac{\sigma_n^s}{e} \Delta \varepsilon_c. \quad (13)$$

Here, σ_n^s is the surface electrical conductivity; $\varphi_s(\pm a)$, $\varphi_m(\pm a)$ are the electrical potentials for semiconductor and metal surfaces, respectively; $\mu_n^s(\pm a)$ is the surface chemical potential of electrons; μ_m is the chemical potential of metal; $\Delta \varepsilon_c$ is the energy gap between the bottom of the conducting band of the semiconductor and the metal conduction band, at the semiconductor-metal contact.

Finally, the electrical potential $\varphi_s(x)$ is determined from Poisson equation if quasi-neutrality is absent:

$$\frac{d^2 \varphi_s(x)}{dx^2} = -4\pi\rho, \quad (14)$$

where $\rho(x) = -e[\delta n'(x) - \delta p'(x)]$ is the bulk charge density.

The continuity of electrical and electrochemical potentials at the $x = \pm a$ should serve as a boundary condition for equation (14):

$$\begin{aligned} \varphi_s(\mp a) &= \varphi_m(\mp a) \\ \tilde{\varphi}_s(\mp a) &= \tilde{\varphi}_m(\mp a) \end{aligned} \quad (15)$$

These potentials are discussed in the next section.

III. INHOMOGENEOUS THERMODYNAMIC EQUILIBRIUM DISTRIBUTIONS OF ELECTRICAL AND CHEMICAL POTENTIALS

First of all, let us consider the energy diagram of thermoelectric circuit elements which are not joined yet into a single whole (see Fig. 2).

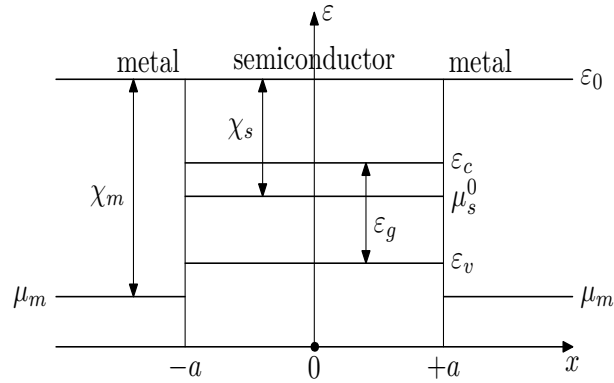


FIG. 2: Energy diagram before joining semiconductor and metal in circuit. ε_0 is the vacuum level; χ_s , χ_m are semiconductor and metal work functions; ε_c , ε_v are the bottom of conduction band and the top of valence band in semiconductor, respectively; μ_s^0 , μ_m are the chemical potentials for semiconductor and for metal, ε_g is the band gap.

Electron and hole concentrations in bipolar semiconductors are represented by the following well known expressions:³

$$\begin{aligned} n_0(T^*) &= \gamma_n(T^*) \exp \left[\frac{\mu_n^0(T^*)}{T^*} \right] \\ p_0(T^*) &= \gamma_p(T^*) \exp \left[\frac{\mu_p^0(T^*)}{T^*} \right]. \end{aligned} \quad (16)$$

Here, $\mu_n^0(T^*) = \mu_s^0$; the hole chemical potential is related to the electron chemical potential μ_n^0 by the expression (2); $\gamma_{n,p}(T^*) = \frac{1}{4} \left(\frac{2m_{n,p}T^*}{\pi\hbar^2} \right)^{3/2}$ are the electron and hole density of states at the bottom of the conduction band and at the top of the valence band; $m_{n,p}$ are the electron and hole effective masses.

A new thermodynamic equilibrium state arises after the creation of a circuit like that shown in Fig. 1, but in the absence of temperature difference ΔT . This state is characterized by a common temperature T^* , and a common electrochemical potential $\tilde{\varphi}(x) = \varphi(x) - \mu_s^0/e$, where $\varphi(x)$ is the electrical potential that arises as a result of charge redistribution between semiconductor and metal, due to the difference in work function.

Usually, one can disregard this charge redistribution in the metal, as it takes place within some atomic layers and one may consider that whole charge is concentrated at the metal surface. The semiconductor charge redistribution essentially depends on the correlation between semiconductor thickness and the Debye radius $r_d^2 = T^*/4\pi e^2 n_0(T^*)$ (for simplicity, we omit the dielectric constant).

The condition of quasi-neutrality is fulfilled if $a^2 \gg r_d^2$. It is characterized by the charge redistribution only in the layers close to the semiconductor surface. The thickness of these layers is about r_d and for typical semiconductors is approximately equal to 10^{-5} – 10^{-7} cm. The change of charge concentration $\delta n_0(T^*)$ in these layers is small in comparison with the equilibrium concentration. At the same time, this redistribution creates a highly appreciable electric field. The concentration distribution in the semiconductor is represented schematically in Fig. 3.

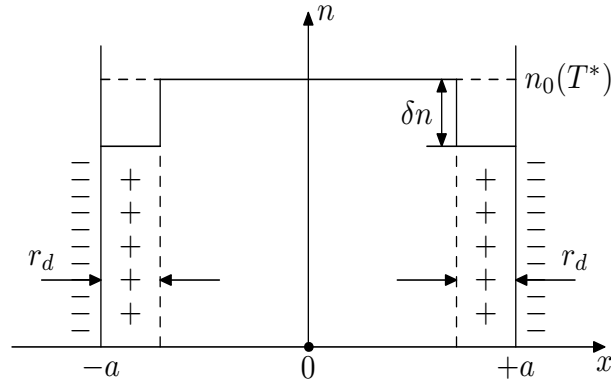


FIG. 3: Distribution of electron concentration in semiconductor near the contact ends with metal $x = \mp a$, at $\chi_s < \chi_m$. Typical value of electron concentration $n_0 = 10^{16} \text{ cm}^{-3}$ and 10^{12} cm^{-3} . Signs (+) and (-) point the charge distributions in the quasi-neutral case ($r_d \rightarrow 0$)

In the limiting case of a long sample ($r_d \rightarrow 0$), as it is implied in the quasi-neutrality model, the double electrical layer is generated, and electrical potential undergoes a gap, which is shown in Fig. 4. The contact voltage arises.

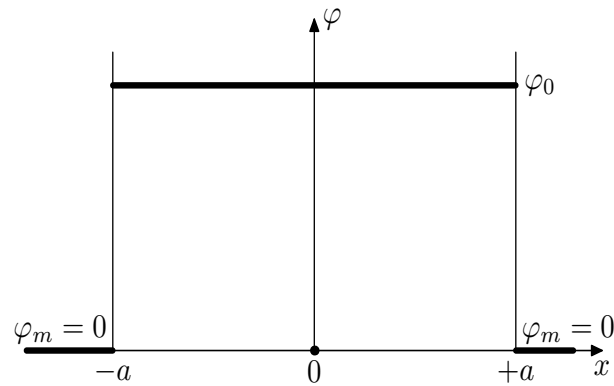


FIG. 4: Contact voltage in the quasi-neutral approximation.

The energy diagram of the circuit in this case is represented in Fig. 5.

The solution of Poisson's equation is not required under quasi-neutrality approximation and the contact voltage φ_0 (the potential of metal is equal to zero), can be found from the condition of equality of electrochemical potential on

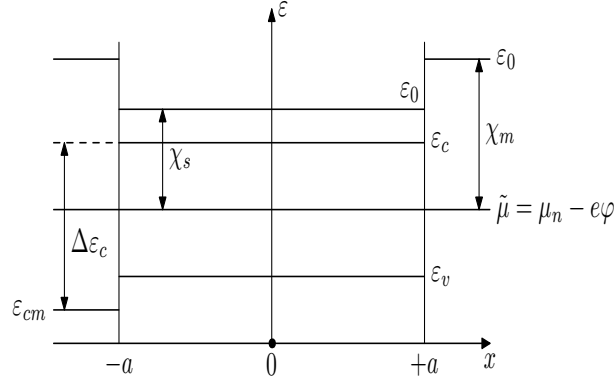


FIG. 5: Energy diagram once equilibrium state has been reached. ε_{cm} is the bottom of metal conduction band, $\Delta\varepsilon_c$ is the energy gap between the bottom of semiconductor conduction band and metal conduction band.

the semiconductor-metal contact (see Fig. 5):

$$\varphi_0 = \frac{1}{e} [\mu_n^0(T^*) - \mu_m - \Delta\varepsilon_c] \quad (17)$$

The appearance of term $\Delta\varepsilon_c$ is explained by the need of choosing a common reference energy level. We took as reference point, the bottom of the conduction band.

A completely different case can be watched in semiconductors which thicknesses are about (or less than) the Debye radius ($a^2 \lesssim r_d^2$), i.e. when the quasi-neutrality condition is absent. Now, the charge redistribution takes place in the whole semiconductor's bulk and the double charge layer does not appear (see Fig. 6).

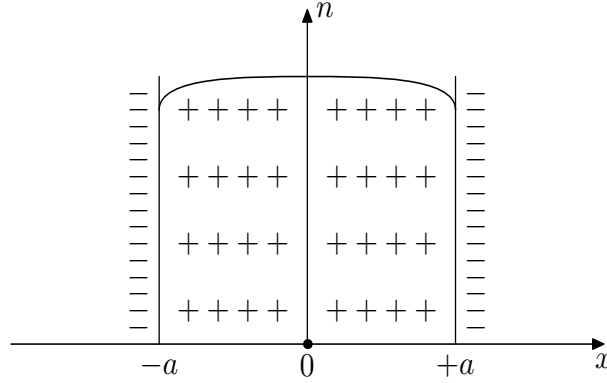


FIG. 6: Distribution of charge in the absence of quasi-neutrality.

Electrical potential is continuous at every point including the points $x = \mp a$. These continuities form boundary conditions (15) to Poisson's equation.

Let us write the distributions of chemical potentials, electron and hole concentrations in the following form:

$$\begin{aligned} \mu_n(x) &= \mu_n^0(T^*) + \delta\mu'_n(x) \\ \mu_p(x) &= \mu_p^0(T^*) + \delta\mu'_p(x) \\ n(x) &= n_0(T^*) + \delta n'_0(x) \\ p(x) &= p_0(T^*) + \delta p'_0(x), \end{aligned} \quad (18)$$

where $\delta\mu'_n(x)$, $\delta\mu'_p(x)$, $\delta n'_0(x)$, $\delta p'_0(x)$ are unknown functions.

We can consider that $\delta\mu'_n(T^*)/T^* \ll 1$, if the difference between work functions is a small one $(\chi_m - \chi_s)/\chi_m \ll 1$, or if the temperature T^* is a high one.

Then, from

$$n(x) = \gamma_n \exp \left[\frac{\mu_n^0(T^*)}{T^*} \right] \exp \left[\frac{\delta\mu'_n(x)}{T^*} \right] = n_0 \left[1 + \frac{\delta\mu'_n(x)}{T^*} \right],$$

it follows that

$$\delta n'_0(x) = \frac{n_0}{T_*} \delta \mu'_n(x). \quad (19)$$

By analogy,

$$\delta p'_0(x) = \frac{p_0}{T_*} \delta \mu'_p(x). \quad (20)$$

We examine the equilibrium state [see Eq. (2)], thus

$$\delta \mu'_n(x) = -\delta \mu'_p(x) \quad (21)$$

and

$$\delta p'_0(x) = -\frac{p_0}{T_*} \delta \mu'_n(x). \quad (22)$$

In this case, Poisson's equation is reduced to

$$\frac{d^2 \varphi(x)}{dx^2} = \frac{1}{er_d^2} \delta \mu'_n(x), \quad (23)$$

Here, $r_d^2 = T^*/4\pi e^2(n_0 + p_0)$, $\varphi(x)$ is the potential distribution in the semiconductor.

The electric current absence condition leads to a correlation between electrical and chemical potentials:

$$\frac{d\varphi(x)}{dx} = \frac{1}{e} \frac{d\mu'_n(x)}{dx}. \quad (24)$$

Solving Eqs. (23,24) simultaneously, we obtain:

$$\begin{aligned} \delta \mu'_n(x) &= C_1 e^{x/r_d} + C_2 e^{-x/r_d} \\ \varphi_0(x) &= \frac{1}{e} \left(C_1 e^{x/r_d} + C_2 e^{-x/r_d} \right) + C_3 \end{aligned} \quad (25)$$

where $C_{1,2,3}$ are yet to be fixed.

To determine them, the constancy of the electrochemical potentials and the continuity of the electrical potential at the boundaries $x = \pm a$ may be used:

$$\begin{aligned} \pm \varphi(\pm a) \mp \frac{1}{e} [\mu_n^0(T^*) + \delta \mu'_n(\pm a) - \mu_m] \pm \frac{\Delta \varepsilon_c}{e} &= 0, \\ \varphi(\pm a) &= 0. \end{aligned} \quad (26)$$

After taking into account the values for the previously undefined constants, we get:

$$\begin{aligned} \varphi(x) &= \varphi_0 \left[1 - \frac{ch(x/r_d)}{ch(a/r_d)} \right], \\ \delta \mu'_n(x) &= -e\varphi_0 \frac{ch(x/r_d)}{ch(a/r_d)}. \end{aligned} \quad (27)$$

The distribution $\varphi(x)$ [see Eq. (27)] is shown in Fig. 7.

It can be seen that the electrical potential distribution is quite different from the distribution when quasi-neutrality is present. The conception of contact voltage lacks of meaning in general, and exists only at $r_d \ll a$.

The energy diagram of the circuit is represented schematically in Fig. 8.

IV. FERMI QUASI-LEVELS AND GENERAL EXPRESSIONS FOR THERMO-E.M.F. UNDER QUASI-NEUTRALITY CONDITION

From the previous section, it is clear that electrical potential distribution and chemical potential are strongly different if quasi-neutrality is present or absent (even for the case $\Delta T = 0$). Therefore, later on this paper we will

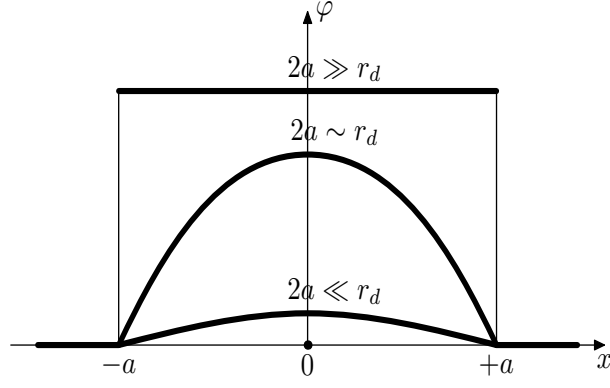


FIG. 7: Distribution of the electrical potential for different semiconductor lengths.

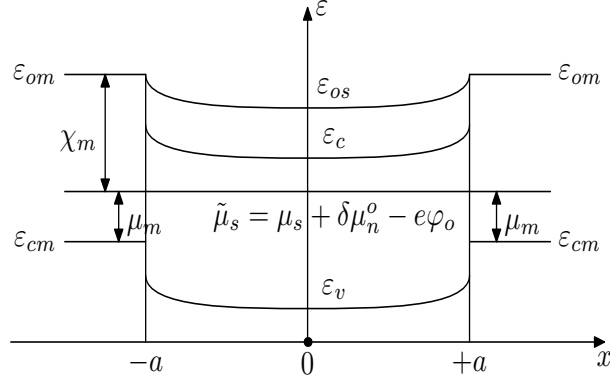


FIG. 8: Energy diagram in the absence of the quasi-neutrality condition. ε_{om} is the vacuum level for both metal and semiconductor.

restrict to quasi-neutrality case only. The opposite situation, when quasi-neutrality is absent, is treated somewhere else.

It is important to understand the double role of temperature inhomogeneity in the construction of a thermo-e.m.f. theory. On the one hand, it is the cause of inhomogeneity in electrical, chemical potentials, and concentration in homogeneous semiconductors. On the other hand, temperature, namely its gradient, determines the thermodynamic force causing particle motion within the sample [terms $\alpha_{n,p} \nabla T$ in Eqs. (5)]. This understanding allows to imagine the process of forming thermo-e.m.f. and thermoelectric current in several stages.

At the first stage, the temperature is the same and equal to T^* at all points of the thermoelectric circuit. Only contact voltage appears in the vicinity of surfaces $x = \mp a$. This situation was described in the previous section in detail.

At the second stage, we suppose that temperature difference ΔT is created between planes $x = \mp a$ and temperature distribution is given by the function (3). The metal chemical potential does not depend on temperature and remains unchanged, the chemical potential and the carrier concentration of semiconductor are the only ones that changes. The initial inhomogeneous electron and hole potentials, and their concentrations, are formed at this stage:

$$\begin{aligned} \mu_{n,p}(x) &= \mu_{n,p}^0(T^*) + \delta\mu_{n,p}^0(x) \\ n_0(x) &= n_0(T^*) + \delta n_0(x), \\ p_0(x) &= p_0(T^*) + \delta p_0(x) \end{aligned} \quad (28)$$

where $\delta\mu_n^0(x)$, $\delta\mu_p^0(x)$, $\delta n_0(x)$, $\delta p_0(x)$ are inhomogeneous additions to equilibrium chemical potentials and equilibrium concentrations. These additions arise due to inhomogeneous temperature [see Eq. (3)]. In spite of this, we suggest that ∇T , as a force, has not “switched on” yet and the carriers are immovable.

At the third stage ∇T is in the condition of “switched off” too, but electrons and holes are free and redistributed due to diffusion flux, and built-in thermoelectric field appears. The electrochemical potentials become common and constant and “equilibrium” state is reached. Inverted commas are used here because it is impossible to use the term “equilibrium” in presence of a temperature field (3). This situation is similar to the formation of inhomogeneous

chemical potential and concentration in the inhomogeneously doped semiconductor: at some point, inhomogeneously distributed donors (for example), give electrons to conduction band and form the initial electron distribution. In the next moment, this distribution changes due to arising diffusion current and internal electric field. As a result, the equilibrium state of inhomogeneous distributed charge carriers is established. The main difference of this example from a distribution that has been observed in the temperature field, is that this is the true equilibrium distribution.

The processes included in the second and third stages were described in Ref. 2, so we do not consider them here in detail and we only use some results. Let us note that at this stage, concentration only determines equilibrium concentration which is used under recombination process description.

At the last stage, the terms $\alpha_{n,p} \frac{dT}{dx}$ are “switched on,” the new additional chemical, electrical potentials, and concentration distributions appear and the thermoelectric current flows through the circuit.

Let us present the concentrations and chemical potentials in this case as follows:

$$\begin{aligned} n(x) &= n_0(T^*) + \delta n_0(x) + \delta n(x) \\ p(x) &= p_0(T^*) + \delta p_0(x) + \delta p(x), \\ \mu_n(x) &= \mu_n^0(T^*) + \delta \mu_n^0(x) + \delta \mu_n(x) \\ \mu_p(x) &= \mu_p^0(T^*) + \delta \mu_p^0(x) + \delta \mu_p(x) \end{aligned} \quad (29)$$

where²

$$\begin{aligned} \delta n_0(x) &= n_0(T^*) \left\{ \left[\frac{\mu_n^0(T^*)}{T^*} - \frac{3}{2} \right] \frac{\Delta T}{T^*} \frac{x}{2a} + \frac{\delta \mu_n^0(x)}{T^*} \right\} \\ \delta p_0(x) &= p_0(T^*) \left\{ \left[\frac{\mu_p^0(T^*)}{T^*} - \frac{3}{2} \right] \frac{\Delta T}{T^*} \frac{x}{2a} + \frac{\delta \mu_p^0(x)}{T^*} \right\} \\ \delta \mu_n^0(x) &= -\frac{d\mu_n^0(T^*)}{dT^*} \frac{\Delta T}{2a} x \\ \delta \mu_p^0(x) &= -\delta \mu_n^0(x). \end{aligned} \quad (30)$$

The spatial charge redistribution in turn leads to the electric potential change:

$$\varphi(x) = \varphi_0 + \delta \varphi_0 + \delta \varphi_1(x) + \delta \varphi(x). \quad (31)$$

Here²

$$\begin{aligned} \delta \varphi_0 &= \frac{1}{e} \delta \mu_n^0(-a) \\ \delta \varphi_1 &= -\frac{1}{e} [\delta \mu_n^0(-a) - \delta \mu_n^0(x)]. \end{aligned} \quad (32)$$

If the condition of quasi-neutrality is imposed $[\delta n(x) = \delta p(x)]$ then it is easy to get that

$$\delta \mu_p(x) = \frac{n_0(T^*)}{p_0(T^*)} \delta \mu_n(x). \quad (33)$$

Now, the expressions for electron and hole currents are:

$$\begin{aligned} j_n(x) &= \sigma_n \left\{ -\frac{d}{dx} \left[\delta \varphi(x) - \frac{1}{e} \delta \mu_n(x) \right] - \alpha_n \frac{dT}{dx} \right\} \\ j_p(x) &= \sigma_p \left\{ -\frac{d}{dx} \left[\delta \varphi(x) + \frac{n_0(T^*)}{p_0(T^*)} \frac{\delta \mu_n(x)}{e} \right] - \alpha_p \frac{dT}{dx} \right\}. \end{aligned} \quad (34)$$

Substituting these expressions into Eqs. (6) we get the following system of equations:

$$\begin{aligned} \frac{d^2 \delta \varphi(x)}{dx^2} - \frac{1}{e} \frac{d^2 \delta \mu_n(x)}{dx^2} &= -e \frac{n_0(T^*)}{T^*} \frac{\delta \mu_n(x)}{\tau \sigma_n} \\ \frac{d^2 \delta \varphi(x)}{dx^2} + \frac{1}{e} \frac{n_0(T^*)}{p_0(T^*)} \frac{d^2 \delta \mu_n(x)}{dx^2} &= +e \frac{n_0(T^*)}{T^*} \frac{\delta \mu_n(x)}{\tau \sigma_p}, \end{aligned} \quad (35)$$

where

$$\tau = \frac{\tau_n \tau_p}{\tau_n + \tau_p}, \quad (36)$$

and times τ_n, τ_p were determined in Eq. (8).

The solution of system (35) is:

$$\begin{aligned} \delta\mu_n(x) &= C'_1 e^{\lambda x} + C'_2 e^{-\lambda x} \\ \delta\varphi(x) &= \frac{\beta^2}{e\lambda^2} \delta\mu_n(x) + C'_3 x + C'_4, \end{aligned} \quad (37)$$

Here,

$$\begin{aligned} \lambda^2 &= \frac{\sigma_n + \sigma_p}{\sigma_n \sigma_p} \frac{n_0(T^*) p_0(T^*)}{n_0(T^*) + p_0(T^*)} \frac{e^2}{\tau T^*}, \\ \beta^2 &= \frac{\sigma_n p_0(T^*) - \sigma_p n_0(T^*)}{\sigma_n \sigma_p [n_0(T^*) + p_0(T^*)]} \frac{e^2 n_0(T^*)}{\tau T^*}. \end{aligned} \quad (38)$$

Constants $C'_{1,2,3,4}$ should be determined from boundary conditions (9) and (13).

After some mathematical manipulation, we arrive to general expressions for the total current in bipolar semiconductors:

$$j_0 \left(\frac{2}{\sigma_n^s} + \frac{L}{\sigma_m} + \frac{2a}{\sigma_n + \sigma_p} \left[1 + \frac{\sigma_p / \sigma_n}{\lambda a \coth(\lambda a) + \lambda^2 \tau a S} \right] \right) = 2a \left[\frac{E_1}{\lambda a \coth(\lambda a) + \lambda^2 \tau a S} - E \right],$$

where

$$\begin{aligned} E_1 &= \frac{\sigma_p (\alpha_p - \alpha_n)}{\sigma_p + \sigma_n} \frac{dT}{dx}, \\ E &= \frac{\alpha_n \sigma_n + \alpha_p \sigma_p}{\sigma_n + \sigma_p} \frac{dT}{dx} \end{aligned} \quad (39)$$

Terms $2/\sigma_n^s$ and L/σ_m determine the contact electric resistance and the resistance of metal section, respectively.

Let us compare now this expression with the general Ohm's law

$$j_0 \mathcal{R} = \mathcal{E}, \quad (40)$$

where \mathcal{R} is the total circuit resistance per cross section unit, \mathcal{E} is e.m.f.

We can state that,

$$R_s = \frac{2a}{\sigma_n + \sigma_p} \left(1 + \frac{\sigma_p / \sigma_n}{\lambda a \coth(\lambda a) + \lambda^2 \tau a S} \right) \quad (41)$$

is the bipolar semiconductor resistance, and

$$\mathcal{E} = 2a \left[\frac{E_1}{\lambda a \coth(\lambda a) + \lambda^2 \tau a S} - E \right] \quad (42)$$

is the thermo-e.m.f.

The electron and hole Fermi quasi-levels have the following general form:

$$\begin{aligned} \tilde{\varphi}_n &= -a \left[\left(\frac{j_0}{\sigma_n + \sigma_p} + E \right) \frac{x}{a} - \frac{j_0 L}{2\sigma_m a} + \frac{j_0 \frac{\sigma_p}{\sigma_n(\sigma_n + \sigma_p)} - E_1}{a\lambda \coth \lambda a + \lambda^2 a \tau S} \frac{\sinh \lambda x}{\sinh \lambda a} \right] \\ \tilde{\varphi}_p &= -a \left[\left(\frac{j_0}{\sigma_n + \sigma_p} + E \right) \frac{x}{a} - \frac{j_0 L}{2\sigma_m a} - \frac{j_0 \frac{1}{\sigma_n + \sigma_p} - \frac{\sigma_n}{\sigma_p} E_1}{a\lambda \coth \lambda a + \lambda^2 a \tau S} \frac{\sinh \lambda x}{\sinh \lambda a} \right] \end{aligned} \quad (43)$$

which shows that they are really different and this confirms our initial assumptions.

From expressions similar to Eqs. (19, 20) and (37), it is easy to obtain the concentrations of nonequilibrium carriers,

$$\delta n(x) = \delta p(x) = \frac{ea}{T^*} \frac{n_0(T^*)p_0(T^*)}{n_0(T^*) + p_0(T^*)} \frac{\sigma_n + \sigma_p}{\sigma_n} \frac{j_0 \frac{1}{\sigma_n + \sigma_p} - \frac{\sigma_n}{\sigma_p} E_1}{a\lambda \coth \lambda a + \lambda^2 a \tau S} \frac{\sinh \lambda x}{\sinh \lambda a} \quad (44)$$

It is important to emphasize that in the proposed approach to thermoelectric transport, thermo-e.m.f. depends not only on electron and hole thermoelectric powers and electric conductivities, but also on the carriers' life time and surface recombination rate. If bulk and/or surface recombination processes are intensive enough ($S \gg S_0 = \frac{n_0 + p_0}{\sigma_n + \sigma_p} \frac{T\sigma_p^2}{e^2 a n_0 p_0}$ and/or $\tau \ll \tau_0 = \frac{e^2 a n_0}{T} \frac{\sigma_n + \sigma_p}{\sigma_n \sigma_p}$) then the thermo-e.m.f. is given by

$$\mathcal{E} = -2a \frac{\alpha_n \sigma_n + \alpha_p \sigma_p}{\sigma_n + \sigma_p} \frac{dT}{dx} \quad (45)$$

i.e. we obtain the well-known result³ for thermo-e.m.f.

On the contrary, when surface and bulk recombinations are quite weak ($S \ll S_0$, $\tau \gg \tau_0$) then we arrive to another result:

$$\mathcal{E} = -2a\alpha_n \frac{dT}{dx}. \quad (46)$$

It is important to note that result (46) concerns both n -type and p -type semiconductors.

Only electrons take part in producing a thermo-e.m.f. in the absence of recombination. This can be this way, only because $j_p = 0$ under $R = 0$, $R_s = 0$ [see Eqs. (6,9)], and the total current j_0 coincides with the electron current j_n . Thus, the thermo-e.m.f. can change sign in p -type semiconductors when both surface and bulk recombination rates decrease.

Let us note that it is possible to rewrite the condition of weak recombination ($\tau \gg \tau_0$) and weak surface recombination ($S \ll S_0$) in the form

$$\begin{aligned} a &\ll \lambda^{-1}, \\ S &\ll \frac{lv_T}{a} \end{aligned} \quad (47)$$

respectively, where l is momentum free length, v_T is the thermal mean velocity.

As it was shown in Ref. 8, surface recombination velocity in epitaxial layers $n - Cd_xH_{1-x}Te$ is $S \sim 10^3$ cm/s at room temperature. As $v_T \sim 10^7$ cm/s, $l \sim 10^{-5}$ – 10^{-6} cm, surface recombination becomes non-effective if $2a \ll 10^{-2}$ cm [see Eq. (47)] (from the point of view of non-equilibrium carriers appearance). If the condition $2a \ll \lambda^{-1}$ takes place, at the same time, the non-equilibrium carriers will play the main role in formation of thermo-e.m.f.

We attract attention upon the fact that bipolar semiconductor resistance and thermo-e.m.f. depend not only on electron and hole electrical conductivities, as it is usually considered, but on recombination rates as well.

The semiconductor resistance takes the usual form:

$$R_s = \frac{2a}{\sigma_n + \sigma_p}, \quad (48)$$

only in the case of strong bulk and/or surface recombinations. In general, it is impossible to calculate the semiconductor resistance independently of full current and thermo-e.m.f.

It should be mentioned that, within the framework of the model considered here, the semiconductor resistance takes the same form as in Eq. (41) in the absence of temperature gradient but in the presence of an external voltage.⁹

Figs. 9 and 10 show the bulk recombination ($\lambda a \sim 1/\sqrt{\tau}$) dependence of total current j_0 and semiconductor resistance R_s respectively. The dependence of Fermi quasi-levels on the surface (S) and bulk recombination is illustrated in Fig. 11. As seen from Figs. 9-10, the total current and the semiconductor resistance depend essentially on the electron-hole recombination rate. It is important to note that for a p -type semiconductor the total current can change direction in dependence of the recombination rate.

Let us pay attention that the Fermi quasi-level of electrons becomes a non-monotonous function of coordinates [see curve (2) in Fig. 11] under small bulk and surface recombination rates. As far as we know, it is the only case when Fermi quasi-level depends on coordinate nonmonotonically.

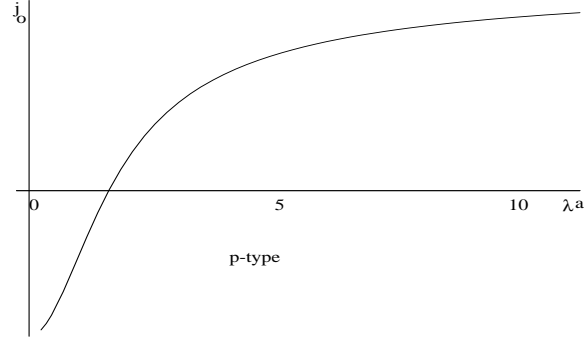


FIG. 9: j_0 as function of λa when $S = 0$ in arbitrary units.

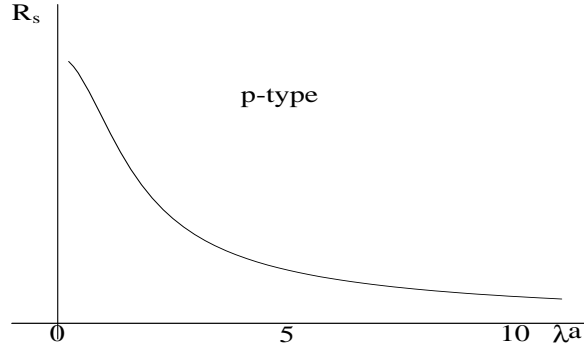


FIG. 10: R_s as function of λa when $S = 0$ in arbitrary units.

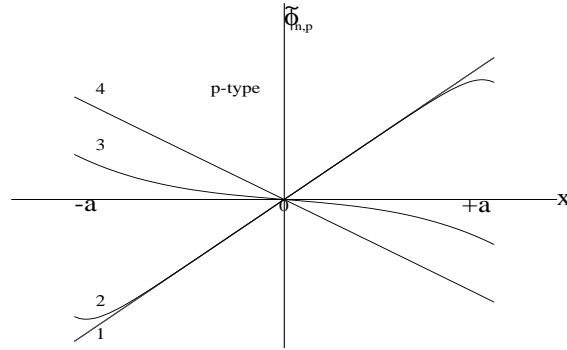


FIG. 11: Fermi quasi-levels for holes $\tilde{\varphi}_p(x)$ (1) and electrons $\tilde{\varphi}_n(x)$ with small (2), intermediate (3), and big (4) life time when $S = 0$ in arbitrary units.

V. CONCLUSION

The area of application of the stated theory is wider and comprehends more complex problems than those solved in the present work. For example when current flows in a closed circuit formed by a current source, p -type semiconductor and connecting metal wires, it is necessary to take into account the effects described in the present work.⁹ The above stated theory shows that essential increase of temperature in n -type semiconductor with large life times and small surface recombination rates does not lead to noticeable changes of thermo-e.m.f. That happens because holes do not contribute to the formation of Seebeck effect, even if its concentration is large enough. This fact can be of essential importance to increase the figure of merit of thermoelectric devices (thermo-generators, thermo-refrigerators).

In general, electron and hole temperatures do not coincide and are not linear functions of coordinates,¹⁰ so their

temperature distributions should be determined by solving the set of energy balance equations for subsystems of electrons, holes, and phonons with the appropriate boundary conditions.

Let us note that the ideas stated in works [1,2] and developed in the present work have found an ulterior development in Ref. [11,12]. At present, experimental works^{13,14,15} have appeared based in the model presented by us. At present, these first results are the initial based on this theory and allow us to think in optimizing the parameters of thermoelectric devices.

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- * Electronic address: gurevich@fis.cinvestav.mx
 - † Electronic address: logvinov@fis.cinvestav.mx
 - ‡ Electronic address: vin@ire.kharkov.ua; Permanent address: Institute for Radiophysics and Electronics, Academy of Sciences of Ukraine, Kharkov 310085, Kharkov 310085, Ukraine.
 - § Electronic address: gespejo@fis.cinvestav.mx
 - ¶ Electronic address: oleg.titov@aleph-tec.com
 - ** Electronic address: meriuts@kpi.kharkov.ua
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